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[Title of Invention] Method of making high strength poly ethylene fiber

[Abstract]

[Objective] Objective of this invention is to provide a method of solvent removal for obtaining high strength poly ethylene fiber that has higher strength than that in the existing methods in the dry spinning method.

[Constitution] Method of spinning in which the solvent is positively removed by blowing heated gas in the spinning chimney prior to stretching in the first stretching tank the polymer solution that was extruded from the spinning die.

Figure: See Fig. 1 at the end of text.

[Claims of the Patent]

[Claim 1] Method of making high strength poly ethylene fiber having a strength of over 35 g/ d by the following processes: The mixture containing 5 ~ 50 wt parts of the ultra high molecular weight poly ethylene polymer and 95 ~ 50 wt parts of volatile solvent is heated for dissolving; the dissolved substance is spun out and, thereafter, the solvent is removed positively; next, stretching is done.

[Claim 2] Method of making high strength poly ethylene fiber in Claim 1 in which heated gas is used to remove the solvent positively.

[Claim 3] Method of making high strength poly ethylene fiber, the method being characterized by that, at the time of removing the solvent positively in Claim 2, the solvent is removed with the gas stream whose temperature and air gas velocity are adjusted at least in two steps.

[Claim 4] Method of making high strength poly poly ethylene fiber, the method being characterized by that, at the time of conducting the stretching in Claim 1, the stretching is conducted while the solvent is being removed.

[Detailed Description of the Invention]

[0001]
[Field of Application in Industry] This invention is related to the high strength poly ethylene fiber that is suitable for use that requires high strength, e.g. the composite reinforced material, rope, fishing line, bullet-proof material, etc.

[0002]
[Existing Technology] In the existing methods of making the high strength poly ethylene fiber, the technique of so called [gel spinning method] in which the ultra high molecular weight polymer is dissolved in a solvent and then is spun is disclosed in, for example, Kokai Patent Publication No. 47922 – 1985 and Japan Patent Publication No. 24887 – 1989. In the existing technology, however, it is necessary that the solvent is not removed as much as possible in the spinning and, in the case of positively removing the solvent, it is said to be not preferable for stretching as is seen in a comparative example of Patent Publication No. 24887 – 1989.

[0003] As to the technology in which the solvent is extracted or washed positively prior to the stretching, the disclosure is seen in Patent Publication No. 5228 – 1983. In this prior art, also, the solvent was almost not removed until the first cooling was done after the spinning. That the solvent was almost not removed until the cooling was because of the large loss of energy and so an efficient method of production has been being sought. When the cooling and taking up are done while the solvent is almost not removed, it is difficult to remove the solvent completely after the stretching process.

[0004] Also, when the stretching is done at a high temperature while the solvent was almost not removed, fusion occurs and so it is necessary to lower the temperature of the stretching tank. But, at a lower temperature, it is impossible to conduct the stretching at a high stretching ratio which is required for obtaining the poly ethylene fiber of excellent high strength. Even if the stretching is done in a multiple stages, unless that stretching ratio is made high at the first stage, it is necessary to conduct the stretching in a fairly high stretching ratio in the second stage and thereafter but, as the deformation rate of the polymer becomes greater relative to the relaxation time of polymer and so there was the problem that the stretching could not be done.

[0005]
[The Problem That the Invention Intends to Solve] Based on the problems described above, this invention provides a production technology for making stably the poly ethylene fiber that has high strength.

[0006]
[The Means for Solving the Problem] Thus, this invention provides the method of making high strength poly ethylene fiber having a strength of over 35 g / d by the following processes: The mixture containing 5 ~ 50 wt parts of the ultra high molecular weight poly ethylene polymer and 95 ~ 50 wt parts of volatile solvent is heated for dissolving; the

dissolved substance is spun out and, thereafter, the solvent is removed positively; next, stretching is done.

[0007] The invention also provides the method of making high strength poly ethylene fiber in the above described production method in which heated gas is used to remove the solvent positively and the method of making high strength poly ethylene fiber, the method being characterized by that, at the time of removing the solvent positively in the above described method, the solvent is removed with the gas stream whose temperature and air gas velocity are adjusted at least in two steps.

[0008] Also, the invention provides the method of making high strength poly ethylene fiber, the method being characterized by that, in the stretching process of the above described production method, the stretching is conducted while the solvent is being removed.

[0009] The ultra high molecular weight poly ethylene in this invention is characterized by that its repeating unit is ethylene substantially and it can be a copolymer with a small amount of other monomer such as α- olefin, acrylic acid and their derivatives, vinyl silane and its derivative. Further, it can be a blend of these copolymer themselves, the ethylene homo polymer and copolymer, or the blend with the homo polymer of other α-olefin and, of course, it can be the ethylene homo polymer.

[0010] Such ultra high molecular weight poly ethylene is generally spun by the previously described [gel spinning method]. For example, when the dissolved substance is extruded through the spinning nozzle, the filaments for use in stretching are obtained. From the extruded dissolved substance, the solvent is removed by using heated gas. Temperature of the heated gas is preferably 50 ~ 130 deg C and more preferably 60 ~ 120 deg C. When the temperature is lower than the said range, solvent removal is insufficient and fusion occurs easily at the stretching process. Also, because of the need for lowering the temperature of stretching tank, it is impossible to conduct the stretching in a high stretch ratio in the stretching tank. Also, if the temperature is higher than the said range, physical properties of the fiber drop. As for the gas velocity, 0.2 ~ 2.0 m/ sec, preferably 0.5 ~ 1.5 m/ sec is used. If the gas velocity is lower than the said range, solvent removal is difficult and, also, if the gas velocity is higher, non-uniformity of the fiber increases.

[0011] Also, when the gas stream is used in 2 or more stages of temperature and velocity, the gas stream temperature of the first stage is 10 ~ 50 deg C, preferably 20 ~ 40 deg C. Lowering the temperature below the said range is difficult in terms of the facilities and, also, there is the danger of cooling the nozzle. Also, when the gas temperature is higher than the said range, it is difficult to obtain the fiber having good strength. The gas stream temperature at the stages after the first stage is 60 ~ 130 deg C, preferably 90 ~ 120 deg C. If the temperature is lower than the said range, solvent removal is insufficient and fusion occurs easily in the stretching process and, if the temperature is higher than the said range, this causes the degradation of the polymer. As for the gas velocity, 0.2 ~ 2.0 m/ sec, preferably 0.5 ~ 1.5 m/ sec is used. If the gas velocity is lower than the said range,

solvent removal is difficult and, also, if the gas velocity is higher than the said range, non-uniformity of the fiber increases.

[0012] The positive removal of solvent that is referred to in this method of production means removing more than 40 %, preferably more than 50 % of the solvent. If the solvent content is higher than that which is defined as said above, fusion occurs easily in the stretching process and, if the stretching temperature is lowered in order to prevent the fusion, stretchability drops and so the stretching rate in the first stretching process can not be raised and, consequently, the fiber of high strength can not be obtained.

[0013] The unstretched, formed body that is obtained in this way is stretch- processed. In this invention, the stretching operation is conducted in one stage or in multiple stages of 2 or more stages. Stretch ratio is 2 ~ 10 in each stretching tank and, in particular, the stretching operation can be conducted at a ratio of 3 ~ 8. When the multiple stage stretching in 2 stages or more is conducted, the temperature at a stage is set higher than that of the previous stretching tank.

[0014] An example of the method of making the high strength poly ethylene fiber of this invention is shown in the process diagram of Fig. 1. In Fig. 1, 3 is the nozzle and the solution prepared by heating and dissolving the ultra high molecular weight poly ethylene in the volatile solvent is spun out from 3 and, prior to the stretching, more than 40 % of the solvent is removed positively by heated gas. The yarn that passed the spinning chimney is sent to the stretching tank on line through the driving roller 4. The stretching tank is heated close to the melting point of the substance being stretched and, at the same time when stretching is being done, the residual solvent is also removed and the taking up is done by the driving roller 6. The poly ethylene filament that was taken up is stretched in one or more stages when necessary.

[0015] Process diagram of another suitable example of the method of making poly ethylene fiber of this invention is shown in Fig. 2. In Fig. 2, as to the arrangement of spinning nozzle, driving roller and stretching tank, there is no difference from Fig. 1 but the characteristic feature of this example is that, when the dissolved substance immedatey after the spinning passes through the chimney, the solvent is being removed by the gas stream that is controlled in two stages of temperature and gas velocity. According to this method, the gas temperature of the first stage is set lower than that of the second stage and, by doing so, the solidification is done in the state where a large amount of solvent is contained and, thereafter, by setting the temperature of gas stream of the second stage higher, the solvent is removed positively and, consequently, a better fiber structure is formed. Also, the stretching can be done to a high stretch ratio in the stretching tank. The evaluations in this invention were conducted by the following sequence.

[0016] (Strength) For the strength in this specification, [Tensilon] that was made by Orientech Co. was used. With a sample of 200 mm length, at a stretching rate of 100 %/min, the stress – strain curve was measured at the atmospheric temperature of 20 deg C and relative humidity of 65 % and the stress at the breaking point of the curve was

determined as the strength (g/d). Here, for each value, the average value of 10 measurements was used.

[0017] (Limiting viscosity) Using 135 deg C decalin and Uberrode type capillary viscosity tube, specific viscosity of various dilute solution was measured and the plot of this viscosity against concentration was made and, from the straight line obtained by least square approximation of this plot, the limiting viscosity was determined from the extrapolated point to the origin of the line. At the measurement, antioxidant (trade name [Yoshinox BHT] made by Yoshitomi Seiyaku) was added by 1 wt % with respect to the polymer (For the polymer, when the raw material polymer was a powder, the powder itself was used and, when it was a bulk or yarn sample, the sample was divided or cut into a length of about 5 mm). The solution for measurement was prepared by dissolving the sample at 135 deg C by stirring for 4 hours.

[0018]
[Examples of Application] In the following, the invention is explained by examples of application but the invention is not limited to the examples of application.

Example of Application 1
10 wt parts of ultra high molecular weight poly ethylene that has a limiting viscosity of 18.5 and 0.8 pieces of methyl branches per 1000 carbon atoms of the main chain and 90 wt parts of decahydro naphthalene were mixed into a slurry and this was fed to the screw type extruder (30 mm ϕ). From the extruder, the dissolved substance was extruded from the nozzle of 0.7 ϕ, 96 holes at the temperature of 175 deg C. After this, the spun yarn was exposed to the heated gas of temperature 90 deg C and gas velocity of 1.0 m/ sec in the spinning chimney to remove the solvent while the yarn was taken up by a driving roller at 75 m/ min. Solvent content of the yarn coming out of the spinning chimney was 76 wt parts. Thus, 65 % of the initial solvent could be removed. The unstretched yarn that was obtained in this way was stretched to a stretching ratio of 3 in the first stage stretching tank that was set at a temperature of 135 deg C on line while the solvent was being removed. In the stretched yarn obtained, the residual solvent was less than 1 %. The yarn that was stretched in the first stage was stretched in the second stage stretching tank that was set at 145 deg C to a stretch ratio of 5.5 at a high stretching rate of 250 m/ min and the stretching could be done up to a ratio of 5.5 and the high strength poly ethylene fiber of strength 45 g/ d could be obtained.

[0019] Example of Application 2
The slurry preparation and the extrusion condition were same as indicated in Example of Application 1. But, in the solvent removal, the gas stream temperature was divided into 2 stages to conduct the spinning. Thus, to the mixed dissolved substance immediately after the spinning, the gas stream of temperature 30 deg C and gas velocity 1 m/ sec was blown in the spinning chimney of 1 m length at the first stage and, after this, the gas stream of temperature 120 deg C and gas velocity 1 m/ sec was blown in the spinning chimney of 1 m length at the second stage. Solvent content of the unstretched yarn coming out of the spinning chimney was 75 wt parts and, thus, 60 % of the initial solvent content could be removed. To this, the stretching was conducted at the same condition as in Example of

Application and the stretching could be done up to a ratio of 5 and the high strength poly ethylene fiber of strength 50 g/ d could be obtained.

[0020] Comparative Example 1
Under the same condition as in Examples of Application, the dissolved substance was extruded from the nozzle and, after this, in the spinning chimney, the gas stream of temperature 25 deg C and gas velocity 1.0 m/ sec was blown. The unstretched yarn coming out of the spinning chimney contained 85 wt parts of solvent. When this unstretched yarn was stretched at the condition that is indicated in Example of Application 1, fusion occurred. Also, when the temperature of the stretching tank was lowered down to 100 deg C, stretching could not be done to a stretch ratio of 3. Therefore, in the first stage stretching tank, stretching was done at a temperature of 100 deg C and stretch ratio of 2. When this was subjected to the second stage stretching at the same stretching condition as in the examples of application, stretching could be done up to a stretch ratio of 6 but, as to the total stretch ratio (first stage stretch ratio x second stage stretch ratio), only a lower stretch ratio than that of the stretched yarn of the examples of application could be obtained and one could obtain only the poly ethylene fiber of strength of 33 g/ d.

[0021]
[Effectiveness of the Invention] In the dry spinning method of this invention where the polymer solution is spun out from the spinning die to form the yarn, the solvent is positively removed in the spinning chimney before the stretching is conducted in the stretching tank and, by this, the fiber having superior properties than that in the previously known technology can be made stably.

[Brief Description of the Figures]

[Fig. 1] is the schematic diagram of the production apparatus that is due to the method of making of this invention.

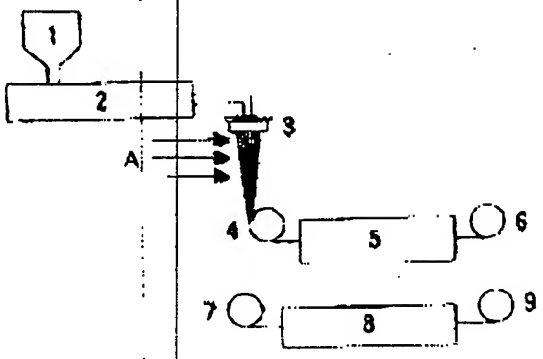
[Fig. 2] is the schematic diagram of the production apparatus that is due to the method of making of this invention.

[Explanation of the codes]
1: Slurry tank; 2: Extruder; 3: Nozzle; 4, 6, 7, 9: Driving rollers;
5: First stretching tank; 8: Second stretching tank;
A: Headed gas; a: heated gas 1; b: heated gas 2

Figures. [Fig. 1] and [Fig. 2]

See the figures in the next page

[Fig. 1]



[Fig. 2]